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BIORESISTANCE OF FOAM-GLASS CRYSTAL MATERIALS TO FILAMENTOUS FUNGI

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The bioresistance of foam-glass crystal materials is studied. These materials are resistant to the mold fungi *Aspergillus niger*. Mold fungi have an adverse effect on the moisture sorption of a material, which increases after biological action but remains within acceptable limits ($\leq 2.5\%$). The effect of mold fungi on the structural changes in the surface layer of the material is corroborated by IR spectroscopy. The particle size of the crystalline phase, and not the amount, plays the leading role in microdamage to inter pore barriers.

Key words: foam-glass crystal material, bioresistance, filamentous fungi, sorption capacity.

A high-priority direction of research in the development of new materials is the question of their environmental safety, reliability and durability. The role of biological corrosion is estimated to reach 50% in processes resulting in the destruction of materials [1]. Examples of the active effect of micro-organisms on the properties of artificial and natural materials are quite extensively presented in the literature [2, 3]. In [4] it is shown that the rate of decomposition of a number of silicates by some micro-organisms is many-fold higher than that due to inorganic solvents with the actual concentrations found in natural objects.

One of the main participants in biocorrosion processes is mold, whose effect on the performance of construction materials draws a great deal of interest. Research in this field shows that out of the great diversity of microscopic organisms filamentous fungi do the greatest damage to construction materials, articles and structures [5, 6]. These fungi and the products of their metabolism are capable of, if not total destruction of a structure, significantly affecting the properties of the materials used. The adverse effect of mold not only affects the durability of a material but it is also dangerous to humans; very small spores (0.005 – 0.0015 mm in diameter) of mold fungi entering the lungs can cause sicknesses that are very difficult to treat, while larger spores cause allergies and lower immunity. For this reason such research is topical from the standpoints of eco-toxicology and materials durability.

Foam-glass crystal (FGC) materials used for heat insulation obtained by the technology described in [7] were chosen

for the present study. It is known that foam glass is environmentally harmless and safe for humans and is not a nutrient medium for fungi, mold or micro-organisms. Several factors, which can alter bioresistance, distinguish FGC material from foam glass: the structure factor — presence of micro- and nanosize particles of a residual crystalline phase in the inter pore barriers of the foam material and the chemical factor — difference of the chemical composition of the glass phase of the foam material. Carbon is also present in foam-glass materials; it is added as a foaming agent and is a source of nutrients for microscopic fungi.

The objective of the present work is to investigate the fungal-resistance of FGC material interacting with filamentous fungi of the type *Aspergillus niger*, which predominate in biodestruction processes, and to make a comparative analysis with other similar foam materials.

Many factors of the external medium affect the physiological activity and growth of fungi: temperature, acidity, light, moisture, pressure and others. High humidity and lack of air circulation are especially favorable for the growth of fungi on a material. In this case fungi continue to grow until the source of nutrient is completely exhausted, after which the lost colony serves as a source of nutrient for other micro-organisms. In the presence of very little moisture fewer moisture-loving fungi appear on the material initially, after which other forms of fungi appear; the moisture can be brought in by the microbial cells themselves, in which its content is 80% or more [8].

An initial assessment of the resistance to mold fungi was made following GOST 9.049–91 [9] for samples of industrial heat and sound insulation foam- glass, polystyrene concrete

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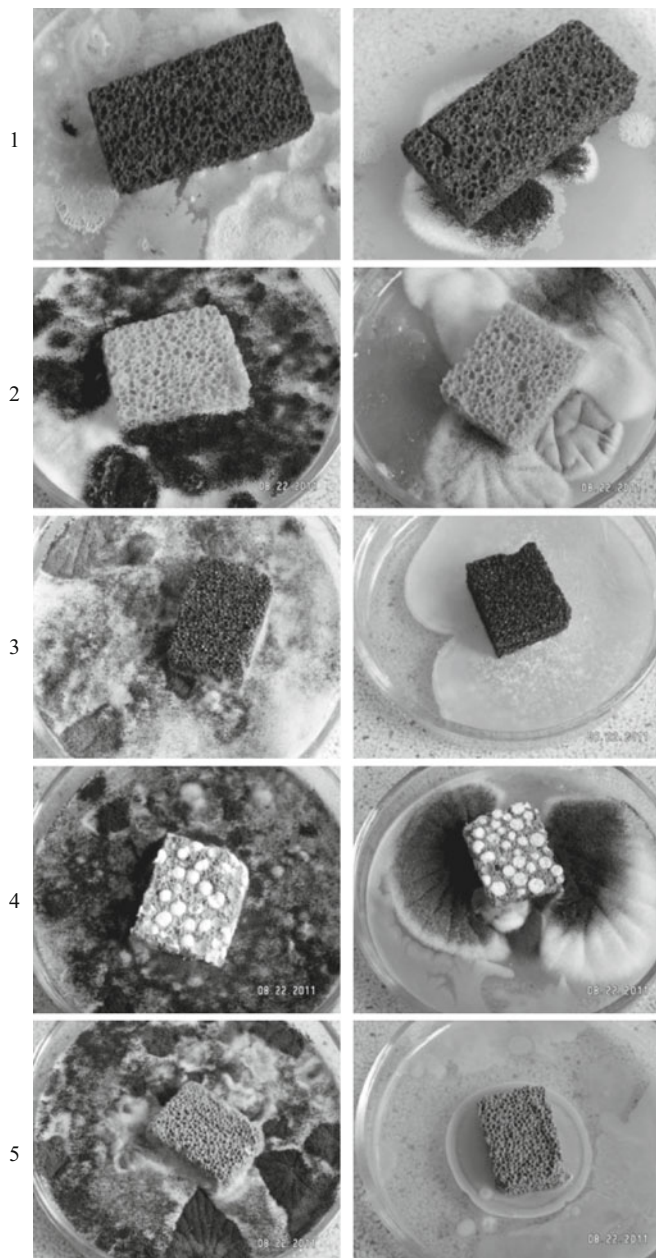


Fig. 1. Photographs of samples after action by mold fungi (left-hand side) and in a medium with no culture (right-hand side): 1) heat-insulation foam glass; 2) sound-insulation foam glass; 3) FGC material; 4) polystyrene concrete; 5) foam concrete.

and foam concrete as well as for laboratory sample of FGC material, whose properties and structure are described in [10].

The crux of the method is to leave the materials contaminated with spores of mold fungi standing under optimal growth conditions and then to evaluate the development of the mold fungi. The method is intended for testing materials and components at the commercial production stage and for replacing raw materials suppliers or changing recipes, if the articles and materials containing them are required to be fungal resistant. The fungal resistance of materials is studied

under conditions simulating mineral and organic contamination.

A pure culture of mold fungi *Aspergillus niger* was seeded on a Czapek–Dox medium in Petri dishes. Fragments of samples were placed on top. Fragments of the experimental materials with similar size and mass were placed on an identical medium without seeding with mold fungi. Control dishes with a culture of the mold fungi *Aspergillus niger* and nutrient medium were arranged in parallel. The materials were kept in a thermostat at 30°C for 14 days, after which traces of growth of mold fungi and spores visible with the naked eye were observed (Fig. 1). Continuous growth of beige-colored cultures with uneven edges and surface was observed on the dishes without the addition of an *Aspergillus niger* culture. Observation under a microscope showed a mixed culture of yeast fungi and gram-positive and -negative micro-organisms. The fungi on the samples were due to the presence of mineral contamination. The characteristics of the samples after the action of the mold fungi and the pH of the medium are presented in Table 1. The control of the nutrient medium remained pure (pH = 6.0) and the control of the culture showed abundant luxuriant growth (pH = 9.0).

The active acidity pH of the medium is important for fungi to grow and develop. For most fungi very acidic and very alkaline reactions of a medium are toxic. The limiting values of the pH above and below which growth stops are 1.0 and 11.0. Most fungi develop best under weakly acidic conditions (pH = 5.0 – 6.0). Research has shown that the hydrogen index of the medium of a sample of sound-insulation foam glass increased to 10.5, and the sample exuded a sharp unpleasant odor, evidently caused by the products of the interaction of *Aspergillus niger* with the newly formed alkaline medium, while for FGC material the hydrogen index remained unchanged.

The results obtained in the course of the experiment show that the experimental samples are fungal resistant; the growth intensity of the fungi on the surface of the samples is estimated to be no more than 2 on the growth scale, i.e., it does not exceed 5% of the surface tested. Sound-insulation foam glass exhibits weak fungal resistance, which is explained by the higher alkalinity of the medium, which is suppressive for the development of microscopic fungi. The degree of growth of fungi on the surface of samples of FGC materials, foam concrete and polystyrene concrete is somewhat higher than for foam glass; this is associated with the presence of external contamination promoting very weak growth of fungi.

Previously it was established that depending on the type of starting material and the heat treatment temperature FGC materials differ by the content of the crystal phase and size of the particles. For this reason, two samples of the FGC material with different content of the crystalline phase (5 and 15%) and a sample of foam glass were chosen to evaluate the effect of these factors. The chemical composition of the glass phase was the same for all samples. The investigations followed the regulations GOST R МЭК 60068-2-10-2009 [11],

TABLE 1. Results for the Fungal Resistance of Foam Materials

Material	Sample characteristics after action by mold fungi	Degree of fun- gal growth on a scale	pH of the medium during sample cultivation	
			no fungi added	fungi added
Heat-insulation foam glass	Traces of growth of mold fungi clearly visible under a microscope	1	6.5	9.0
Sound-insulation foam glass	Spore growth visible with the naked eye is localized in several locations together covering no more than 5% of the surfacel	1	7.0	10.5
FGC		2a	6.0	6.0
Polystyrene concrete		2a	4.5	6.5
Foam concrete		2a	6.0	6.5

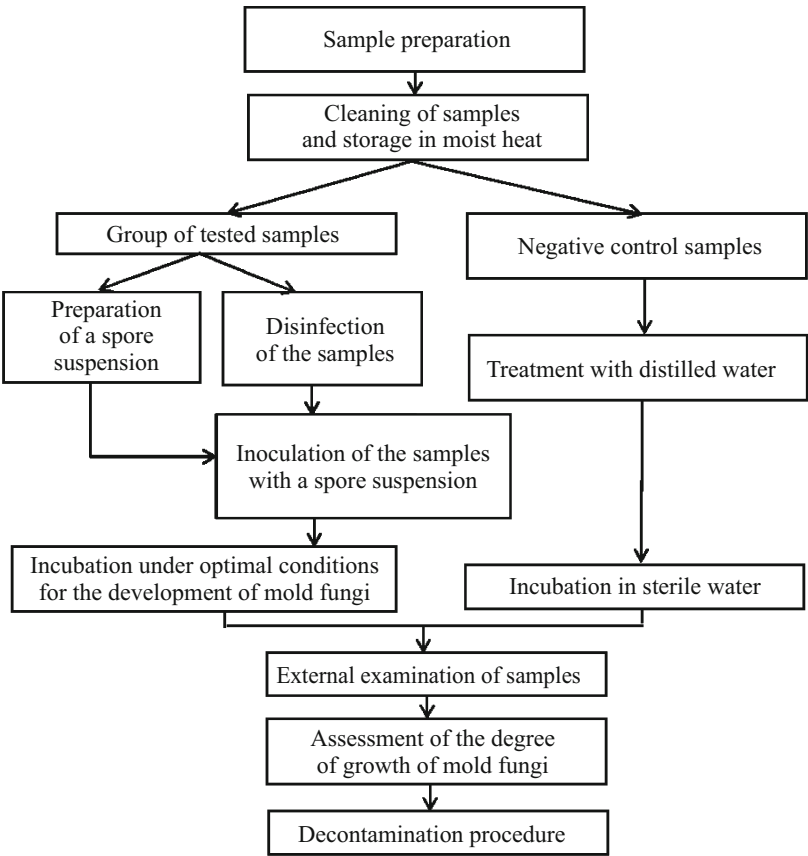


Fig. 2. Scheme for performing tests of samples for fungal resistance.

according to which for tests the articles are contaminated with spores from cultures of mold fungi and incubation is conducted under conditions that are favorable for spores to germinate and mold fungi to grow without a nutrient medium.

The tests were conducted using cultures of mold fungi *Aspergillus niger* following the scheme displayed in Fig. 2. Prepared and pre-cleaned experimental samples were inoculated with mold fungi by spraying in Petri dishes a spore suspension of an *Aspergillus niger* culture and kept for 28 days. Photographs of the control medium and the samples are displayed in Fig. 3. Germination of spores and conidia was not found under a microscope at magnification $\times 50$. Fungal growth was consistent with zero on the growth scale.

It was determined that the mass content of the crystalline phase in an interpore barrier of the foam materials to 15% has no effect on the bioresistance of the material. However, very small fungal growth on the surface of the material is not proof of absence of any effect of micro-organisms on the performance of the material. For this reason, measurements of the sorption capacity of the samples inoculated with a spore suspension and control samples

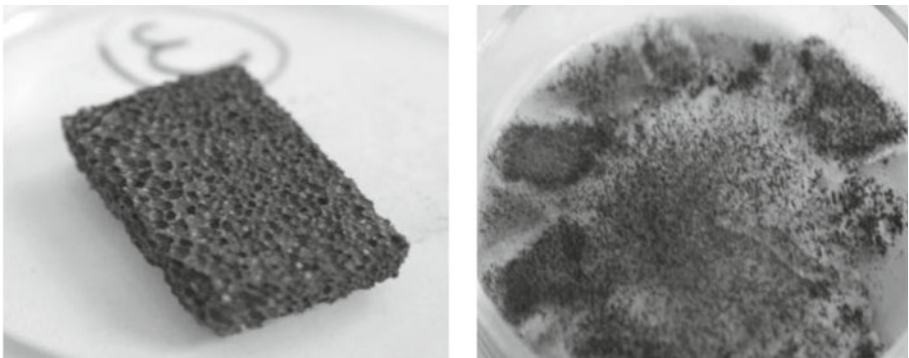


Fig. 3. Photographs of FGC material after the action of mold fungi (left-hand side) and the control medium (right-hand side) (28 days).

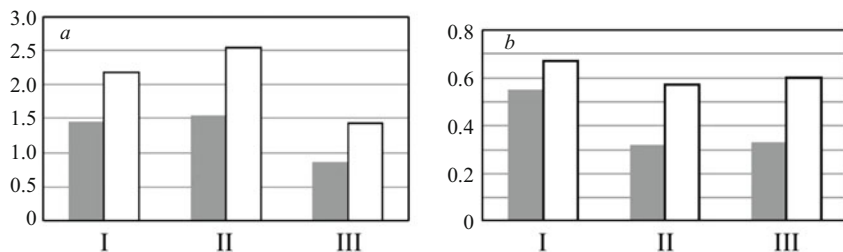


Fig. 4. Histogram of the change in the moisture sorption of foam-glass samples: *a*) after the action of mold fungi; *b*) absence of action by mold fungi; (■) 24 h holding time; (□) 72 h holding time; I, II, III) mass content of the crystalline phase 0, 10 and 15%, respectively.

kept in a sterile medium were performed to evaluate the possible biocorrosion. The tests were conducted by the method of accelerated determination of the moisture sorption by keeping pre-dried (to constant mass) samples in a desiccator above water for 24 and 72 h at temperature $22 \pm 5^\circ\text{C}$ and then weighing [12].

It was determined that mold has an adverse effect on the sorption capacity of porous materials; the moisture content increased several-fold in all samples exposed to mold. For example, for foam glass the moisture sorption increased by factors of 2–3 with 24- and 72-h holding times, respectively. For FGC samples with 5 and 15% crystalline phase this value increased 4–5-fold and 2–3-fold, respectively (Fig. 4). It is necessary to take account of the difference in the size of the particles of the crystalline phase present in a barrier of the foam material. For the sample with the lower mass content of quartz the particle size was about $10\ \mu\text{m}$, while for the sample with 15% quartz the particle size was less than $1\ \mu\text{m}$. This attests to micro-damage to the surface layers of the interpore barrier of the material and to the fact that the size of crystalline particles has a stronger effect on the biocorrosion of the material than the number of particles. However, even after biological action the moisture sorption of the FGC material remains within admissible limits and does not exceed 2.5%.

It is known that water can be present in different structural states in glass [13]. A comparative analysis of IR spectra in the range $400 - 4000\ \text{cm}^{-1}$ (Nicolet 5700 spectrometer) was performed to study the structural changes in the surface layer of foam materials after the action of mold fungi. It was determined that the main differences in the spectra of the experimental samples are observed in the high-frequency IR-range of the spectrum. In all three samples absorption bands ($3712 - 3788\ \text{cm}^{-1}$) corresponding to the stretching vibrations of OH-groups appear after the fungal action. In contrast to foam glass one other new absorption band in the region $2387 - 2308\ \text{cm}^{-1}$, corresponding to the vibrations of hydroxyl groups connected by hydrogen bounds with non-bridge oxygen atoms of isolated silicon-oxygen tetrahedra $[\text{Si}(\text{OR})_4]$ in the spectra of FGC materials [14]. In the interval $800 - 1050\ \text{cm}^{-1}$, which is a characteristic absorption range of isolated groups of tetrahedra $[-\text{SiO}^4]$, the spectra remain but differ in intensity. Specifically, the absorption band at $960\ \text{cm}^{-1}$ increases in intensity after fungal action because the fraction of non-bridge bonds Si–O and the degree of de-polymerization of the structure of the glass phase

of the material increase. New absorption bands appear in the wavenumber range $2103 - 3620\ \text{cm}^{-1}$, which can be attributed to nonassociated OH groups or complexes of the type Si–OH...O–Si. The presence of water and silanol groups on the surface of the material can be determined according to two characteristic absorption bands at 3200 and $1650\ \text{cm}^{-1}$ whose intensity after fungal action increased only for samples with 5% crystalline phase, while in other cases the intensity decreased very little.

These studies of the bioresistance of foam-glass crystal materials have established the following. In accordance with GOST R MÉK 60068-2-10-2009 the experimental samples show fungal resistance with respect to mold fungi *Aspergillus niger*. After the fungal action their degree of growth on the surface of the material is zero. Mold fungi have an adverse effect on the moisture sorption of the material, whose value after biological action increases but remains within admissible limits, not exceeding 2.5%. The effect of mold fungi on the structural changes in the surface layer of the material is supported by IR-spectroscopic data, according to which the degree of depolymerization of the structure of the glass phase increases and hydroxyl groups appear. The size of the particles of the crystalline phase and not the number of these particles plays the main role in the microdamage to the interpore barrier.

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